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OPTIMIZATION OF FERRITIC STEEL POROUS SUPPORTS FOR PROTONIC FUEL CELLS WORKING AT 600°C

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Metal supported protonic fuel cells (PCFC) offer one major advantage over standard solid oxide fuel cells (SOFC) with oxygen conducting electrolytes, namely that the product, water, is produced on the cathode (air) side. This feature simplifies the engineering of the stack, boosts efficiency, and is particularly helpful for a porous metal supported cell because it limits the corrosion of the metal by exposure to water vapor in the anode gas.

In this work, we show the effect of composition and microstructure on the high temperature corrosion and phase stability (formation of sigma phase/Laves phase) of porous alloys. Alloys in the compositional range Fe-20%Cr to Fe-32%Cr were evaluated and the effects of surface modification on corrosion resistance were studied using thermogravimetry, x-ray diffractometry and electron microscopy. The results show that surface modified porous ferritic steels are very promising materials for cost effective protonic fuel cells operating at 600°C.

Keywords: SOFC, Protonic fuel cell, Metal supports, porous alloys, corrosion, protective coating

Introduction:

SOFC's are electrochemical devices to convert chemical energy to electrical energy. SOFCs consist of an anode and a cathode separated by a thin electrolyte. Although the state of the art of SOFCs is based on oxygen conducting electrolytes, recent attention has been also drawn towards proton conducting oxides as electrolytes¹. For proton conducting fuel cells (PCFCs), the electrolyte conducts protons^[2,3]. Typical fuel and oxidant are humidified hydrogen and air, respectively. The protonic conductive fuel cells usually operate at temperatures around 600°C. One of their largest advantages is that steam is produced at the cathode side, without dilution of the fuel which results in higher voltage efficiency^[4,5,6]. Anode supported PCFC's offer reasonable power densities and stabilities⁷. However, as for the SOFC cells, cost reduction are highly desirable and thus metal supported cell constructions should be considered^[8].

Metal supported PCFCs consisting of ceramic layers on metallic supports have many advantages compared to conventional fuel cell technologies, namely good thermal conductivity, improved thermal shock resistance and better mechanical properties; above all they also offer reduced cost compared to all-ceramic based devices^[9]. Porous metal supports are expected to have high potential for mobile applications because of their relatively high resistance to thermal & mechanical stresses^[10]. Also, they enable the use of well-established joining techniques such as welding and brazing^[11]. The criteria for making use of porous metal supports are to improve

oxidation resistance and maintaining relatively low area specific resistance without any mechanical failures. The corrosion rate of porous alloys is very high due to the high porosity & hence, the high surface area. This results in a decrease of porosity and increase in electrical resistance^[12]. The dominant trend for reducing corrosion rate on dense alloys has been to apply protective coatings on their surface^[13].

A limited amount of work has been done to find suitable porous alloys for PCFC applications^[14,15]. This effort has been limited to commercially available ferritic stainless steel alloys with high chromium content (>16 wt%)^[15], as they combine matching coefficients of thermal expansion with formation of low electrical resistive oxide protective scale. So far, no work has been reported on the effect of alloy composition on the oxidation kinetics of the porous alloys. Hence, in the present study, alloys with different chromium and manganese content were produced and evaluated for their corrosion properties. Possible protective coatings were also investigated.

Experimental Procedure

Characterization of the as-sintered tapes:

Four different alloys of different compositions produced by Höganäs AB (Höganäs, Sweden) were chosen for the present study. The alloys contained varying amount of chromium (20-32 wt.%) with some addition of manganese (0.4 wt.%) to induce dual layer formation i.e. inner layer of chromia and outer layer of Mn Cr spinel during high temperature treatment. Notably all the alloys contained low levels of Si and Al impurities. The detailed chemical compositions of the alloys are given in Table 1.

The porous alloys were prepared by Höganäs AB as water atomized powders and sieved through a sieve with an opening of ~53 µm. Thin sheets with a thickness of 0.4 mm (after sintering) were produced by Höganäs AB using tape casting followed by sintering in H₂ at 1250°C.

Table 1. Chemical composition of the sintered tapes.

Target Composition	Fe	Cr	Ni	Mo	Mn	Cu	Si	Al	Nb	W	C	O	N	S
Fe-20%Cr	Bal.	20	0.07	0.02	0.03	0.03	0.08	0.00	0.02	0.00	0.01	0.03	0.01	0.00
Fe-20%Cr-0.4%Mn	Bal.	22	0.03	0.01	0.23	0.02	0.08	0.00	0.02	0.00	0.01	0.03	0.01	0.00
Fe-26%Cr-0.4%Mn	Bal.	27	0.01	0.04	0.30	0.00	0.08	0.00	0.02	0.00	0.01	0.03	0.02	0.00
Fe-32%Cr	Bal.	32	0.02	0.08	0.09	0.00	0.07	0.00	0.13	0.00	0.02	0.04	0.03	0.00

Sample coupons of 15 mm x 15mm from the four different alloys, sintered at 1250°C for 30 minutes in H₂, were used for oxidation studies at 600°C in H₂/3%H₂O atmosphere to evaluate their usefulness as possible supports for high temperature fuel cells, especially for the use on the anode side of the protonic fuel cells operated at 600°C as is the goal for operation of a PCFC.

A solution of yttrium nitrate hexahydrate of 0.1 M concentration was prepared to form the protective coatings on the porous alloys. The samples were impregnated using the nitrate solutions for 1 & 4 iterations and heat treated at 600°C for 2 hours in an atmosphere of H₂/3%H₂O. Also, the samples were pre-oxidised at 800°C for 2 hours in H₂/3%H₂O atmosphere to ensure formation of coherent scale prior to the long term aging tests at 600°C.

The as-received alloys along with the pre-oxidised and Y-coated samples were subjected to oxidation experiments at 600°C for 100 and 200 hours in an atmosphere of H₂/3%H₂O. The initial and final weights of the samples were measured. The samples were characterized using XRD and SEM. For the determination of the specific surface area by BET, a large amount of material, typically 1 m² surface area, were required for achieving reasonable accuracy. The porosity of the oxidised samples was determined from the cross section of the SEM images using the ImageJ program.

Results and Discussion:

The SEM surface image of the as-sintered sheet from Figure 1 shows that the surface is highly porous with large pores with diameters in the range of 20 – 30 µm. The particle size of the alloys is very prominent at higher magnification. Good connection and necking between the stainless steel particles is also observed after the sintering.

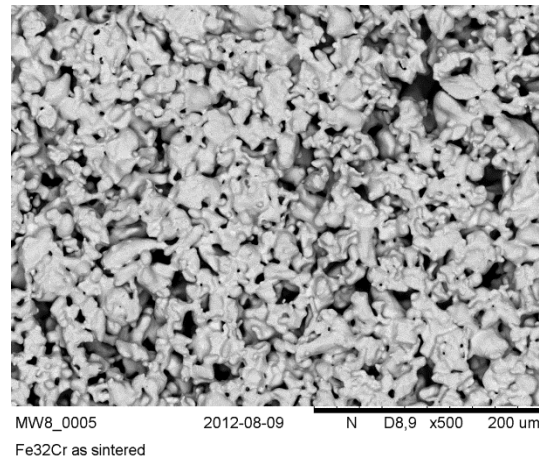


Figure 1. Surface SEM images of Fe-32%Cr.

From the polished cross sections of all of the sintered tapes, total porosities were calculated by an image analysis method. For each type, several images were analysed in an ImageJ program to ensure good statistics of the obtained porosity.

The kinetics of oxide scale growth is usually expressed in weight gain per unit area of samples. However, this methodology is not straight forward for the porous alloys due to the complex geometry and the difficulty in measuring surface area accurately. Hence different approaches have been proposed^[16], for example percentage weight change. In the present study the percentage weight gain is used.

$$\left(\frac{\Delta w}{w_0} \right)_t = 100 \left(\frac{w_1 - w_0}{w_0} \right) \dots \dots \dots \text{Equation 1}$$

where, Δw is the weight change due to the oxidation, w₁ is the sample weight after a time t, hours of oxidation in g, w₀ is the initial sample weight in g.

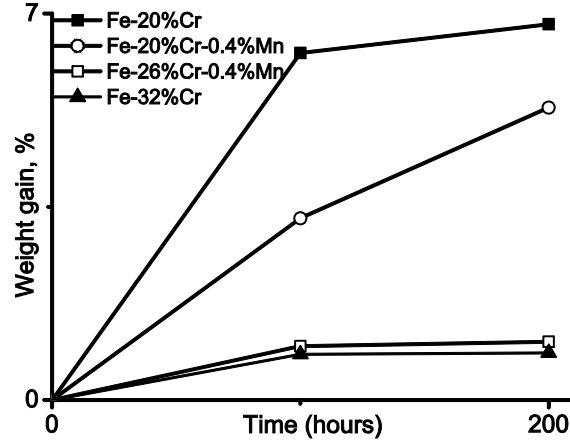


Figure 2. Weight change (%) during oxidation at 600°C in $H_2/3\%H_2O$ atmosphere.

Figure 2 shows the weight change during oxidation at 600°C in $H_2/3\%H_2O$ atmosphere. The initial oxidation up to 200 hours follows parabolic behaviour and is confirmed by longer exposures. This suggests the alloys follow the expected Wagner's theory of high temperature oxidation. The rate of oxidation is found to decrease with increasing Cr content for 20 to 32 wt%, suggesting formation of protective chromia oxide scale. Figure 3 shows the X-ray diffraction analysis on the oxidised alloys after 200 hours at 600°C in $H_2/3\%H_2O$ atmosphere. It shows the formation of Iron diffused chromium oxide ($FeCr_2O_4$) for low Cr content alloys (<26 wt%), even for the alloys with 0.4wt% Mn addition. Whereas the alloys with high Cr content of 32 wt% forms only chromia scale. The diffusivity of Mn and Cr is nearly similar at lower temperature¹⁷. Hence, it does not form any protective Mn-Cr based oxides at 600°C for short duration. However, this point needs further detailed elucidation.

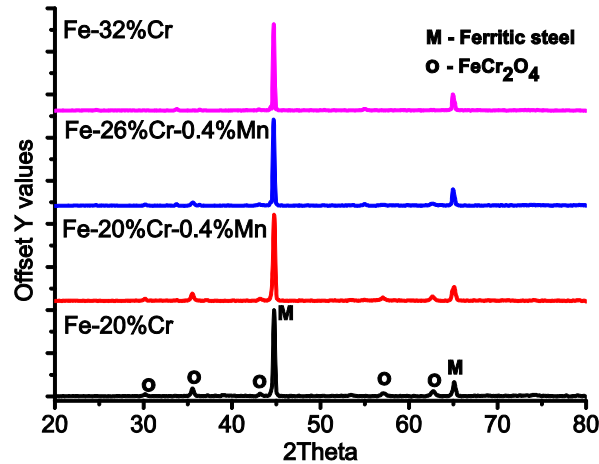


Figure 3. XRD pattern of porous alloys of different compositions oxidised at 600°C for 200 hours in $H_2/3\%H_2O$ atmosphere.

The surface SEM images as shown in Figure 4 confirms the formation of localised discontinuous Fe diffused Chromium oxides for alloys with low Cr content irrespective of Mn addition. Whereas, for alloys with high Cr (> 26 wt%) with or without Mn addition shows uniform, continuous oxide scale formation. Thus, corroborate well with the low % weight gain.

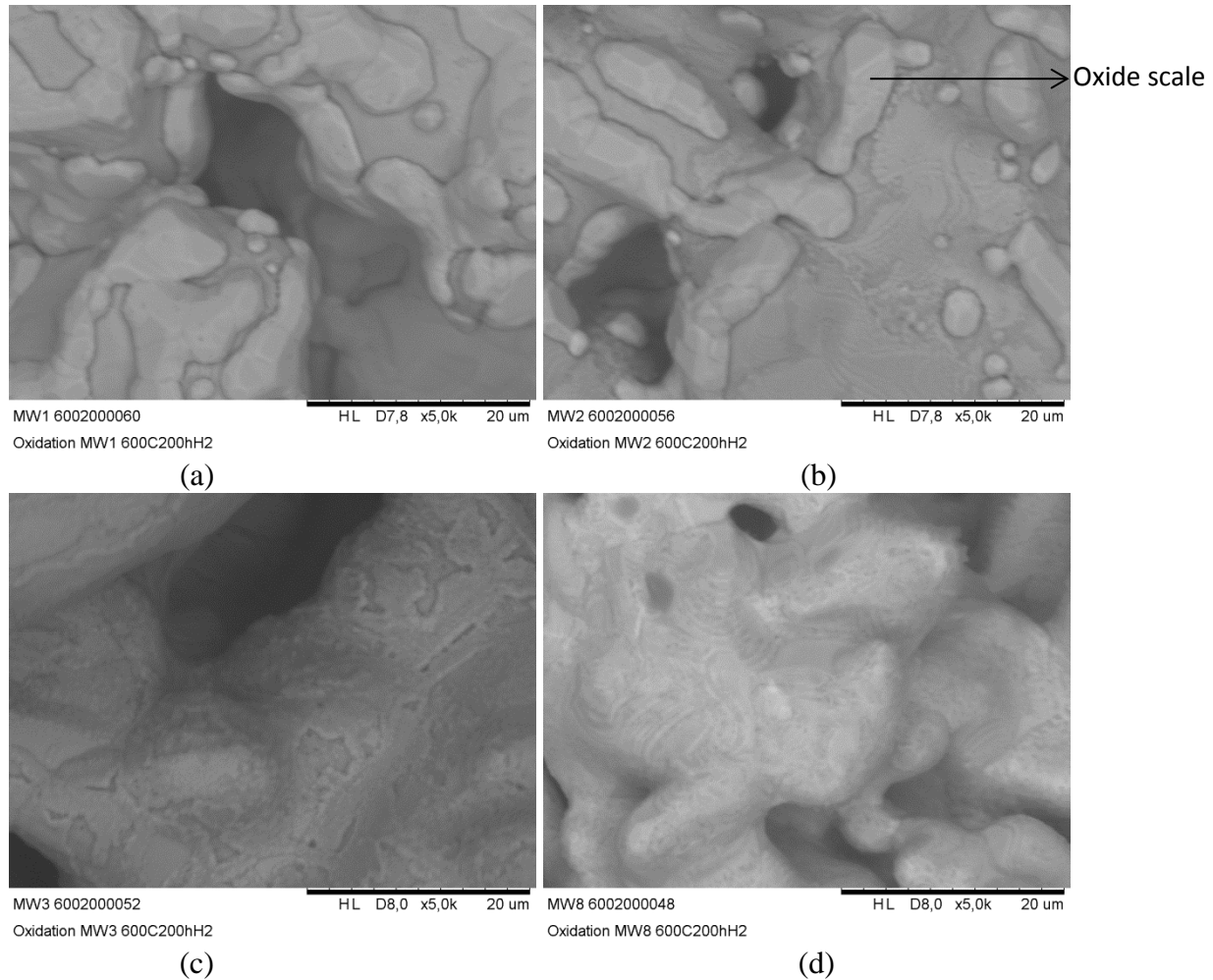


Figure 4: The surface SEM images of the porous alloys of different compositions oxidised at 600°C for 200 hours in $H_2/3\%H_2O$ atmosphere. (a) Fe-20%Cr, (b) Fe-20%Cr-0.4%Mn, (c) Fe-26%Cr-0.4%Mn, (d) Fe-32%Cr

Pre-Oxidation:

The weight gain against oxidation at 600°C in $H_2/3\%H_2O$ atmosphere of the pre-oxidised alloys of different compositions with in situ or internal protective oxide formation is shown in Figure 5. The rate of oxidation is found to have reduced by a factor of 10 due to the pre-oxidation compared to the as-sintered alloys. Alloys with Mn addition have lower oxidation rate compared to the other alloys. On the growing Cr_2O_3 , Mn diffuses two orders of magnitude faster than Cr¹⁸. The diffusivity of Mn is higher than Cr and Fe¹⁹. Hence, alloys with Mn addition forms $(MnCr)_3O_4$ at the periphery. The $MnCr_2O_4$ is more corrosive resistance than Cr_2O_3 . Thus the corrosion resistance of the alloys is improved with small addition of Mn.

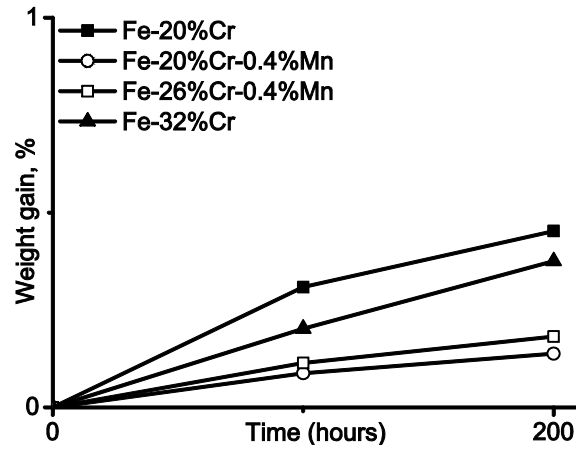
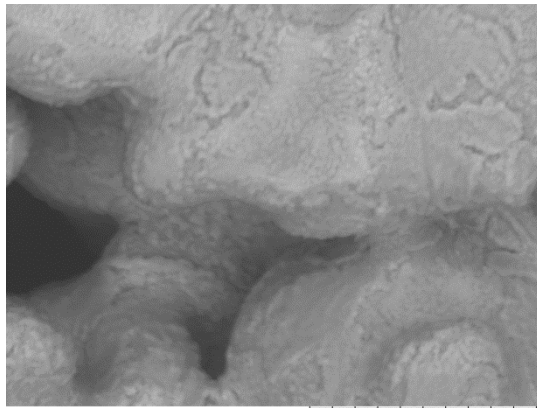
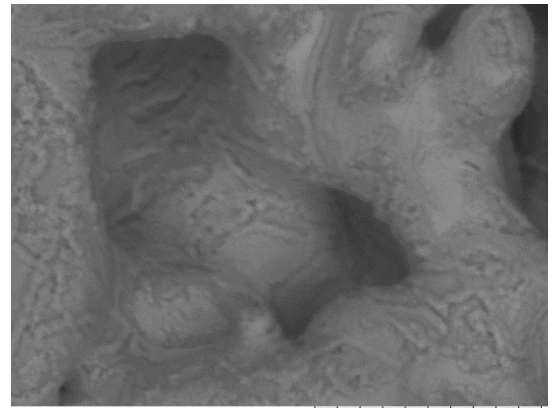


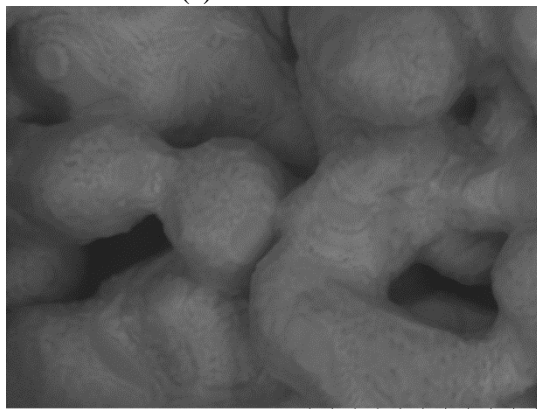
Figure 5. Weight change (%) during oxidation at 600°C in $H_2/3\%H_2O$ atmosphere of samples subjected to 2 h heat treatment at 800°C in $H_2/3\%H_2O$ atmosphere



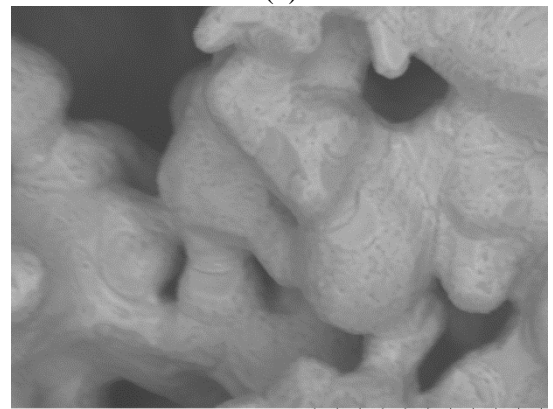
(a)



(b)



(c)



(d)

Figure 6. The surface SEM images of the pre-oxidized porous alloys of different compositions after 200 hours in $H_2/3\%H_2O$ atmosphere at 600°C. (a) Fe-20%Cr, (b) Fe-20%Cr-0.4%Mn, (c) Fe-26%Cr-0.4%Mn, (d) Fe-32%Cr

Yttrium protective coatings:

The alloys were impregnated with yttrium (Y) and heat treated to form a protective external oxide. Figure 7 shows significant reduction in % weight gain during oxidation at 600°C in $H_2/3\%H_2O$ atmosphere after the application of Y. Again, alloys containing Mn addition have lower oxidation rate compared to the other alloys. The XRD patterns of the Y coated alloys does not show any significant Y peaks, as the amount of Y is well under the detectable limits of the technique. Also the intensities of the additional peaks are very low suggesting lower amount of corrosion products compared to the as-sintered oxidised alloys.

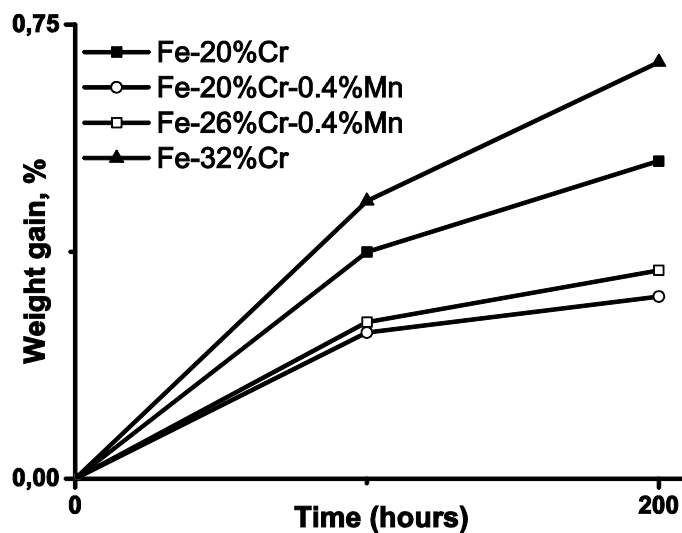
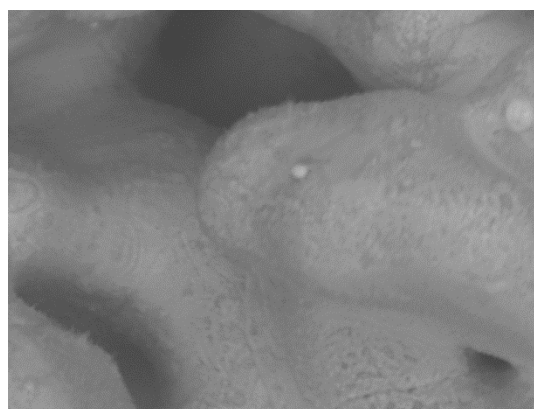


Figure 7. Weight change (%) during oxidation at 600°C in $H_2/3\%H_2O$ atmosphere of samples impregnated with Yttrium and heat treatment at 600°C for 2h in $H_2/3\%H_2O$ atmosphere



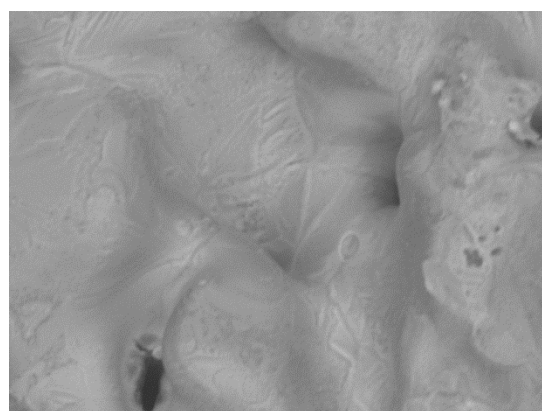
Y4X200hMW10024 2014-05-26 HL D7,4 x5,0k 20 um
Y 4X 200h MW1

(a)



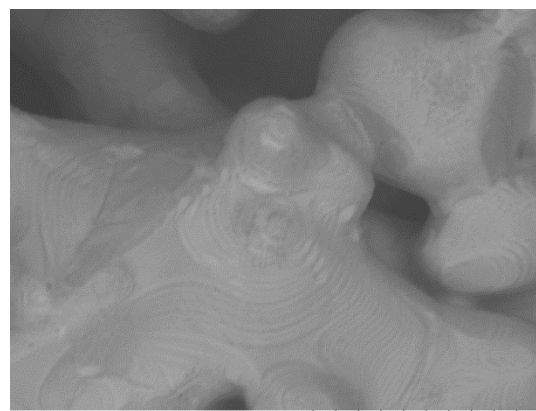
Y4X200hMW20032 2014-05-26 HL D7,4 x5,0k 20 um
Y 4X 200h MW2

(b)



Y4X200hMW30036 2014-05-26 HL D7,3 x5,0k 20 μm
Y 4X 200h MW3

(c)



Y4X200hMW80040 2014-05-26 HL D7,4 x5,0k 20 μm
Y 4X 200h MW8

(d)

Figure 8. Surface SEM images of Y coated porous alloys of different compositions, after testing at 600°C for 200 hours in an atmosphere of $H_2/3\%H_2O$. (a) Fe-20%Cr, (b) Fe-20%Cr-0.4%Mn, (c) Fe-26%Cr-0.4%Mn, (d) Fe-32%Cr

Conclusions:

The first initiative to study the effect of porous alloys composition with varying Cr and Mn content has been performed and evaluated within the consortium targeting PCFC applications. Thus alloys requires minimum of 20 wt% of chromium content. Addition of small amount of Mn enhances the internal protective oxide layer and minimises further oxidation. Controlled pre-oxidation or impregnations of rare earth elements such as yttrium using simple techniques have proven again the possibility to improve the oxidation resistance of the porous alloys. Thus, these alloys have the potential to be suitable for protonic fuel cell applications at 600°C on the anode side.

Acknowledgements

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